characterized by a fall of the slope of the current-voltage characteristic and called the anomalous resistance region.[9] As at 77 K (Ref. 10), this behavior could be attributed to the pinch effect. This hypothesis was confirmed not only by the fact that the Bennett criterion was satisfied in the investigated range of high currents,[10] but also by the results of a study of the dynamics of the establishment of a voltage in the constant-current regime (inset in Fig. 3). In H = 0 under the breakdown conditions we observed a clear initial fall at the tops of the pulses (curve 4) reflecting a reduction in the resistance of the sample because of generation of an electron–hole plasma. At high currents, when a negative magnetoresistance was observed, the pulses assumed a shape (curves 5 and 6) typical of the pinch effect[9]: after a fall associated with the plasma generation, the resistance rose because of enhancement of the electron–hole scattering and because of an increase in the rate of bulk recombination of carriers in the course of the pinch effect. As the current increased, the pinch time τ_p, taken to be the time to the establishment of the anomalous resistance or to the first maximum in a periodic process, decreased; moreover, as in the case of InSb (Ref. 9), this decrease obeyed a law close to $\tau_p \propto I^{-1}$ and amounted to $\sim 10^{-7}$ sec, in agreement with the theoretical estimates. In a magnetic field the region representing the establishment of the anomalous resistance (curves 6-8) gradually disappeared from the voltage pulses, indicating suppression of the pinch effect.[9]

[1)]We shall assume that the contribution of holes, which are heavy compared with electrons, to the transport effects can be ignored if the magnetic field is sufficiently weak.

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Translated by A. Tybulewicz

Modifiable thermal donors in silicon in the form of defects with $U < 0$

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(Submitted August 29, 1984; accepted for publication May 4, 1985)

Fiz. Tekh. Poluprovodn. 19, 1935–1939 (November 1985)

The results of an investigation of the equilibrium occupancy function are used to prove the existence of a negative effective correlation energy of oxygen thermal donors in silicon. The energy levels of modifiable centers of two types, formed at different stages of heat treatment, are determined.

Anderson[1] proposed the existence of defects with a negative correlation energy U in order to explain optical, magnetic, and electrical properties of amorphous semiconductors. It has been found that such defects exist also in crystalline semiconductors, as shown first for a vacancy and an interstitial boron atom in silicon.[2,3] We recently demonstrated[4] that heat treatment of SiO crystals at 300–500°C creates oxygen thermal donors with U < 0. However, Hoffman et al.,[5] who investigated energy levels of thermal donors, failed to detect defects of this kind. We therefore decided to provide a more detailed proof that U < 0 characterizes oxygen thermal donors and we shall base this proof on an investigation of the equilibrium occupancy function of such centers.

According to the equilibrium statistics of multiply charged centers in semiconductors,[6] the ratio of the concentration of defects in two charge states differing by unity is

$$\frac{N^{(j)}}{N^{(j-1)}} = \exp\left[\frac{E_F - E(j/j-1)}{kT}\right], \qquad (1)$$

where j is the number of electrons at a given defect; E_F is the Fermi level; $E[j/(j-1)]$ is the level of a defect defined as the difference between the free energies in the charge states j and j − 1.

We shall consider a doubly charged donor. The relationship between the energy of its levels $E(0/+)$ and $E(+/++)$ can be represented by

$$E(0/+) = E(+/++) + U, \qquad (2)$$

where U is the effective correlation energy due to the electron–electron repulsion and due to changes in the free energy of a defect because of elastic relaxation of the lattice, formation of new bonds, etc. If $U < 0$ and $|U| \gg kT$, it then follows from Eq. (1) that for any positions E_F the condition $N^{(+)} \ll N^{(0)} + N^{(++)}$ (i.e., $N^{(0)} + N^{(++)} \simeq N$) is obeyed and the electron occupancy function of such a defect is

$$\frac{N^{(0)}}{N} = \left\{1 + \exp\left[2\frac{E(0/++) - E_F}{kT}\right]\right\}^{-1},$$

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where N is the concentration of the defects and the quantity $E(0/++) = (1/2)[E(0/+) + E(+/++)]$ represents the occupancy of the defect: if $E_F > E(0/++)$, the defect is in the neutral state, whereas for $E_F < E(0/++)$, it is in the doubly ionized state. In this situation as well as in the case of singly charged defects, the temperature dependences of the carrier density exhibit only one "step" due to the ionization of the center. However, the difference between Eq. (3) and the Fermi function, which governs the degree of occupancy of the levels of conventional centers, makes it possible to determine the nature of the investigated defect (the existence of a negative correlation energy $U < 0$) from an analysis of the temperature dependences of the carrier density without recourse to other more complex experiments.[3]

We investigated n-type Si crystals (ρ = 2-100 Ω·cm) prepared by the Czochralski method and containing oxygen in amounts of $(6-8)\cdot 10^{17}$ cm^{-3} and carbon in amounts of $(5-15)\cdot 10^{16}$ cm^{-3}. We determined the temperature (T_{meas} = 77-400 K) dependences of the Hall coefficient and of the electrical conductivity. The carrier densities were calculated allowing for the temperature dependence of the Hall factor. The concentration and parameters of the thermal donors were found from an analysis of the temperature dependences of the carrier density by the application of the conventional method based on the solution of the electrical neutrality equation.[7] The free energy ΔE, the enthalpy ΔH, and the entropy ΔS of the ionization process were calculated from the formula

$$\left(\frac{n}{N_c}\right)^{\alpha}\frac{n-(N_d-N_a)}{(N_d-N_a+\alpha N)-n}=\exp\left[-\alpha\frac{\Delta E^{(\alpha)}}{kT}\right]\equiv\exp\left[\alpha\frac{\Delta S^{(\alpha)}}{k}\right]\exp\left[-\alpha\frac{\Delta H^{(\alpha)}}{kT}\right], \quad (4)$$

where n is the density of free electrons; N_c is the effective density of states in the conduction band; N_d is the concentration of shallow donors; N_a is the concentration of the compensating acceptors; N is the concentration of the thermal donors; α = 1 applies to centers with the usual sequence of the local level; α = 2 represents defects with $U<0$, $\Delta E^{(1)}=E_c-E(j/j-1)\equiv\Delta H^{(1)}-T\Delta S^{(1)}$, $\Delta E^{(2)}=E_c-E(0/++)\equiv\Delta H^{(2)}-T\Delta S^{(2)}$.

Our results were compared with those of Ref. 5 by applying the differential method according to which the positions of the levels and the concentration of the defects can be found from the dependence of the quantity $Y = kT(dn/dF)$ on $F = E_c - E_F$ (Ref. 8). If the levels of the various defects are located sufficiently far from one another, the dependence Y(F) is in the form of spectral bands. In the case of the conventional defects the ordinate of the maximum is $Y_m = N/4$, the abscissa of the maximum is $F_m = \Delta E^{(1)}$, and the half-width of each band is $\delta F \approx 3.5kT$. In the case of defects with $U < 0$, we have $Y_m = N$, $F_m = \Delta E^{(2)}$, and $\delta F \approx 1.8kT$ (Ref. 9).

As a result of heat treatment at 350-500°C we find that Si:O crystals form a series of doubly charged thermal donors which have slightly different parameters. This has been found earlier both for thermal donors with shallow levels ($\sim E_c - 0.05$ and $\sim E_c - 0.15$ eV)[10] as well as for modifiable centers.[11] We shall demonstrate that $U < 0$ in the case of modifiable thermal donors (MTD-1) the properties of which have been studied earlier.[4] The concentration of thermal donors of this type is the highest in the initial stages of heat treatment and this makes them a convenient object of investigation.

Figure 1 shows temperature dependences of the carrier density of a sample of n-type Si in the initial state (curve 1) and after heat treatment at 400°C for 5 h (curves 2 and 3). It should be pointed that determination of the equilibrium temperature dependences of the carrier density in heat-treated crystals presents some difficulty. This is due to the formation of modifiable centers as a result of heat treatment and these centers are characterized by a longer time for the establishment of a thermodynamic-equilibrium distribution between various charge states, which may give rise to a residual conductivity.[4] This residual conductivity appears as a result of an abrupt change in temperature or as a result of illumination of crystals with white light. Therefore, the nature of the temperature dependences of the carrier density in such crystals depends strongly on the cooling and heating regimes. Curve 3 in Fig. 1 was obtained as follows: a sample was illuminated with white light at room temperature and cooled rapidly to 77 K, and the measurements were carried out during heating. Curve 2 was determined by slow cooling of a sample from T = 400 K. In the range T_{meas} = 400-270 K, where the ionization of the MTD-1 centers was observed, the experimental points corresponded to the equilibrium values of the carrier density. At lower temperatures, when modifications in the thermal donors of the

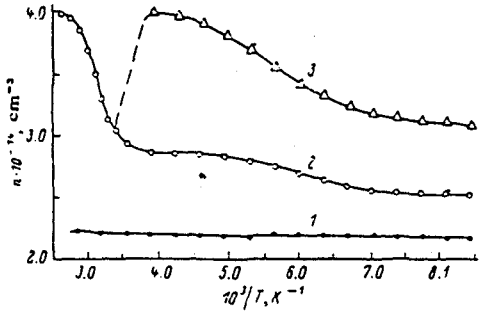

FIG. 1. Temperature dependences of the carrier density in silicon crystals subjected to heat treatment at 400°C for 5 h: 1) original sample; 2, 3) heat treatment at 400°C followed by slow cooling (2) or by quenching to 77 K during illumination with white light (3).

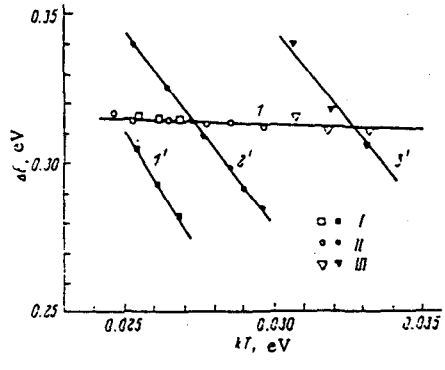

FIG. 2. Temperature dependences of the free energy of ionization of modifiable thermal donors of the first type calculated from Eq. (4) for α = 2 (curve 1) and α = 1 (curves 1'-3') in the case of Si crystals with different carrier densities n_0 (cm^{-3}): I) $\approx 6\cdot 10^{13}$; II) $\approx 2.5\cdot 10^{14}$; III) $\approx 2.5\cdot 10^{15}$.

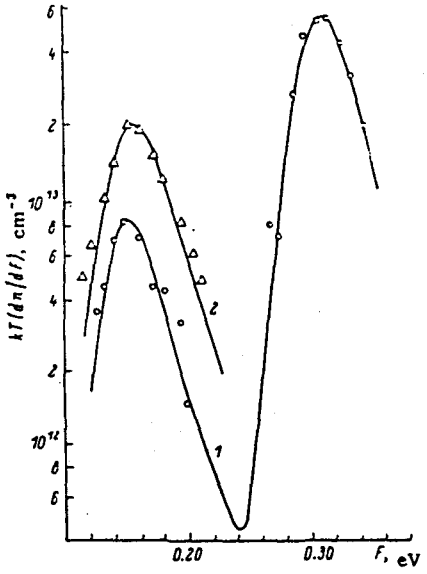

FIG. 3. Dependences of kT(dn/dF) on F, calculated from the temperature dependences of the carrier density plotted in Fig. 1. Here, curves 1 and 2 have the same meaning as curves 2 and 3 in Fig. 1.

second type (MTD-2) began, it was not possible to obtain an equilibrium value of n: the modification time τ of MTD-2 in this material was $\geq 10^5$ sec.

A calculation of the parameters of the MTD-1 centers was made using Eq. (4). The value of α was assumed to be 1 (conventional defect) or 2 (defect with U < 0). The following values of the ionization enthalpy and entropy were obtained: for $\alpha = 1$, we found that $\Delta H^{(1)}_{exp} = 0.63 \pm 0.02$ eV and $\Delta S^{(1)}_{exp} = (11.2 \pm 0.5)k$; for $\alpha = 2$, we found that $\Delta H^{(2)}_{exp} = 0.32 \pm 0.01$ eV and $\Delta S^{(2)}_{exp} = (0.3 \pm 0.3)k$. In both cases the correspondence between the values of n calculated for given parameters of a defect with those determined experimentally was satisfactory (within the limits of the experimental error). Therefore, it was not possible to give immediately an unambiguous answer on the nature of the investigated defects on the basis of the results obtained. However, the value of $\Delta S^{(1)}_{exp}$ was anomalously high, since in the case of defects in silicon the ionization entropy is usually moderate.[12] The large difference between the experimentally determined two expected values of ΔS can be explained by assuming that MTD-1 is a defect with U < 0. In fact, Eq. (3) describing the degree of occupancy of double donors with U < 0 can be regarded as the Fermi function with an effective level $E^{(1)}_{eff} = 2E(0/++) - E_F$. Then, the effective ionization entropy $\Delta S^{(1)}$ is greater than the true value $\Delta S^{(2)}$ by an amount $\sim k \ln (N_c/n)$. It therefore follows that if we assume that $\alpha = 1$ and calculate the parameters of a defect employing the usual occupancy function of local levels and obtain an anomalously high value of $\Delta S^{(1)}$, then we can assume that the defects in question have a negative correlation energy. The final proof of the unsuitability of the Fermi function in the description of the degree of occupancy of such defects can be obtained by showing that $\Delta S^{(1)}$ depends on the carrier density.

Figure 2 shows the temperature dependences of the free energy of ionization of MTD-1 obtained from an analysis of the temperature dependences of the carrier density in crystals with different dopant concentrations. We can

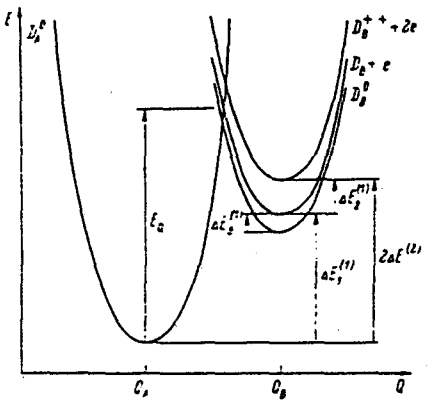

FIG. 4. Configurational-coordinate diagram of MDT-1. $E_a \approx 0.9$ eV is the activation energy of thermal ionization of D^0_A (Ref. 4).

see that $\Delta E^{(2)}_{exp}$ changes relatively slowly with temperature and is independent of n. On the other hand, $\Delta E^{(1)}_{exp}$ depends strongly on temperature and the temperature coefficient equal to $\Delta S^{(1)}_{exp}$ depends on the carrier density in the original crystals in accordance with the law $\Delta S^{(1)}_{exp} \approx k \ln (N_c/n)$. It follows from these results that modifiable thermal donors in silicon are defects with U < 0.

An analysis of the temperature dependences of the carrier density in heat-treated crystals by the differenti method confirms the above conclusion. Figure 3 gives t dependences Y(F) calculated from the temperature dependences of the carrier density shown in Fig. 1 and obtained by applying the numerical differential procedure described in Ref. 8. The dependences Y(F) have tow bar with maxima located at $F_{m1} \approx 0.155$ eV ($T_{m1} \approx 165$ K) a at $F_{m2} \approx 0.315$ eV ($T_{m2} \approx 320$ K). The half-widths of these bands are $\delta F_1 \approx 0.050$ and $\delta F_2 = 0.047$ eV, representing $\sim 3.5kT_m$ and $\sim 1.7kT_m$, respectively.

In accordance with the criterion proposed in Ref. 9 for the determination of the type of defects ($\delta F = 1.8kT_m$ for centers with U < 0, but U < 0, $\delta F = 3.5kT_m$ for the conventional defects), the second level should be attribu to defects with U < 0. However, it should be pointed out that the condition of Ref. 9 is generally insufficient for t identification of the nature of the defect. It follows fron an analysis of the expression for Y obtained from the el trical neutrality equation that the half-width of a band d pends on how strongly does the position of the level var with temperature, i.e., it depends on the ionization entropy. We can readily show that $\delta F \approx (3.5/\alpha)kT_m - \Delta S \delta T$, where $\delta T = T_2 - T_1$ is the difference between the temperatures at the points corresponding to $F_1 = F_m - {}^1/_2\delta F$ and $F_2 = F_m + {}^1/_2\delta F$. However, attempts to accou for the low value of δF in the case of the investigated centers on the basis of the occupancy function of conve tional defects (i.e., on the assumption that $\alpha \approx 1$) gives anomalusly high value of the entropy factor ($\Delta S = 10$–12 and this, as pointed out above, can be regarded as an in dication that the defects are characterized by U < 0.

The properties of defects with U < 0 are exhibited by the modifiable thermal donors MTD-2. The concent tion of these donors obtained after a sufficiently long he treatment reached values much higher than the maximu concentration of MTD-1 ($N^{max}_{MTD-1} \leq 10^{14}$ cm^{-3}). This m it possible to investigate the properties of MTD-2 in cr tals with a lower resistivity and the value of the therm

charge exchange time τ was $\leq 10^4$ sec. The E(0/++) level of the defect was found by us to be $E_c - 0.225 \pm 0.010$ eV. This was practically identical with the thermal donor level $E_c - 0.23$ eV found in Ref. 5. Probably the low relative concentration of the thermal donors with this level in the crystals investigated in Ref. 5 was the reason why the authors of that paper failed to detect defects with $U < 0$.

We shall conclude by noting that the equilibrium temperature dependences of the carrier density can be used only to determine the level E(0/++). Other parameters of modifiable thermal donors can be found by a combined analysis of the quasiequilibrium temperature dependences of the carrier density and of the results obtained in Ref. 4 from a study of the nonequilibrium conductivity relaxation. As shown in Ref. 4, the modifiable thermal donors can occur in two configurations A and B separated by an energy barrier. In view of the considerable height of this barrier, the investigated centers can be "frozen" in the configuration B and their transition from singly to doubly ionized states can be observed, which makes it possible to determine the levels E(+/++) from an analysis of the quasiequilibrium temperature dependences of the carrier density (curve 3 in Fig. 1 and curve 2 in Fig. 3). If we know E(0/++) and E(+/++), we can readily calculate the levels $E(0/+) = 2E(0/++) - E(+/++)$ and the effective correlation energy $U = E(0/+) - E(+/++)$. In the case of MTD-1 we have $E(0/+) \approx E_c - 0.5$ eV, $E(+/++) \simeq E_c - 0.16$ eV, $U \approx -0.35$ eV, whereas for MTD-2, we have $E(0/+) \approx E_c - 0.3$ eV, $E(+/++) \simeq E_c - 0.155$ eV, and $U \approx -0.15$ eV. It follows from the configurational coordinate diagram of MTD-1 (Fig. 4), plotted using the results of Ref. 4, that the E(0/+) level and the value of U are not associated with any specific configuration of the defects, but represent the properties of defects as a whole. The modifiable thermal donors in the configuration B can be regarded as helium-like doubly charged donors and they can be described by their own system of levels $E_B(0/+) = E_c - (0.06\text{–}0.07)$ and $E_B(+/++) = E_c - (0.15\text{–}0.16)$ eV (Ref. 10).

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Translated by A. Tybulewicz

Recombination processes in nonstoichiometric $TlGaSe_2$

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(Submitted October 4, 1984; accepted for publication May 4, 1985)
Fiz. Tekh. Poluprovodn. 19, 1940–1943 (November 1985)

Recombination processes in nonstoichiometric $TlGaSe_2$ crystals were investigated at 77 K. Two recombination levels with depths $E_{cr1} = 1.2$ and $E_{cr2} = 0.95$ eV were observed. The phenomenological parameters of these centers were determined. A study of the photoconductivity and related properties yielded a scheme of photoelectrically active transitions in the band gap of $TlGaSe_2$ crystals.

The compound $TlGaSe_2$ belongs to the class of layer semiconductors of the $A^{III}B^{III}C_2^{VI}$ type. According to Müller and Hahn,[1] the space group of this compound can be C_s^4 or C_{2h}^5. They gave preference to the space group C_s^4. Photoelectric properties of stoichiometric $TlGaSe_2$ crystals have been investigated.[2,3] The results obtained indicated that stoichiometric $TlGaSe_2$ crystals have a low photosensitivity. The photoconductivity of nonstoichiometric $TlGaSe_2$ crystals was investigated earlier[4] under carrier injection conditions. The present paper reports a determination of the scheme of photoelectrically active transitions in the band gap of nonstoichiometric $TlGaSe_2$ crystals.

Our p-type crystals were prepared by the Bridgman–Stockbarger method. An electron-probe microanalysis, carried out using a Camebax unit, showed that in the case of $TlGaSe_2$ there were deviations of the composition from stoichiometry: the deficiency of thallium and gallium was 1.54 and 1.12%, respectively. According to Ref. 5, these deviations from stoichiometry were within the homogeneity range of the compound $TlGaSe_2$. Symmetric contacts were made from a eutectic InGa mixture. The equilibrium density of holes was $(3\text{–}5) \cdot 10^8$ cm^{-3} and the band gap at 77 K was 2.15 eV. An electric field was applied along the layers and light was incident perpendicular to the $TlGaSe_2$ layers. Measurements were made at 77 K. Nonstoichiometric $TlGaSe_2$ crystals had a high photosensitivity. The ratio of the resistivity in darkness and duirng illumination, measured for an illumination intensity of 200 lx at 77 K, amounted to $\sim 10^3$–10^4. All the $TlGaSe_2$ samples prepared for the photoconductivity investigations were found to be photosensitive in the impurity absorption region. Curve 1 in Fig. 1 is the spectrum of the impurity photocurrent with two strong maxima characterized by long-wavelength edges at 0.95 and 1.2 eV (they represent